RE: Hao et al
ord 4296
09/646978
529 Rec'd PCT/PTO 25 SEP 2000

SPECIFICATION

LIGHT-EMITTING MATERIAL AND PRODUCING METHOD THEREOF

TECHNICAL FIELD

The present invention relates to a light-emitting material and a producing method thereof, and more particularly, to an inorganic light-emitting material using a rare-earth element as an exciting agent and having an afterglow time and a producing method thereof.

BACKGROUND TECHNIQUE

A light-emitting material is utilized is mixed in ink or paint to make light emitting paint, and is utilized on a safe sign and a clock board. Conventionally, copper-excited zinc sulfide (ZnS: Cu) was widely used as the light-emitting material. ZnS: Cu has high light-emitting efficiency in the light-emitting spectral region, but its brightness is lowered extremely rapidly, and the visible afterglow time is as short as 20 to 30 minutes. When the ZnS: Cu is exposed to ultraviolet rays in areas exposed to moisture, decomposition and degeneration are generated and the body color of the material darkens. Therefore, there are constraints for using ZnS: Cu outside, and optimal material as a substitute for ZnS: Cu had long been required.

In CN1053807A, a light-emitting material ($m(Sr_{1-x}Eu)O \cdot nAl_2O_3-yB_2O_3$) having long afterglow ability and is laid open. In the above general formula, $1 \leqq m \leqq 5$, $1 \leqq n \leqq 8$, $0.005 \leqq y \leqq 0.35$ and $0.001 \leqq x \leqq 0.1$. The afterglow time of this light-emitting material is in a range from 10 to 20 hours.

In ~~USP5.~~ USP 5,376,303, phosphor having long afterglow ability comprises a compound ($MO \cdot a(Al_{1-b}B_b)_2O_3: cR$).

In this general formula, $0.5 \leqq a \leqq 10.0$, $0.0001 \leqq b \leqq 0.5$, $0.0001 \leqq c \leqq 0.2$, MO is a at least one compound selected from a group consisting of MgO, CaO, SrO and ZuO. R consists Eu and at least one additive rare-earth element selected from a

CL 8/1/03

group consisting of Pr, Nd, Dy and Tm.

In the above-mentioned patent, some phosphors such as $SrO \cdot 2.10 (A1_{0.952}B_{0.048})_2O_3$: 0.005Eu, 0.020Dy (which will be referred to as "A" hereinafter), and $SrO \cdot \cancel{1.025(A1_{0.976}B_{0.024})_2O_3}$ $1.025(Al_{0.976}B_{0.024})_2O_3$: 0.005Eu, 0.015 Dy (which will be referred to as "B" hereinafter) were prepared, and residual light-emitting time and brightness of these phosphors were evaluated in view of afterglow time constant (n) and relative brightness (ZnS: Cu, Cl were evaluated). A measuring result shows that the afterglow time constants of A and B phosphors and ZnS: Cu, Cl are 0.94, 0.86 and 1.26, respectively, and phosphorus brightness after 10 seconds are 144, 220 and 100, respectively, and phosphorus brightness after 20 seconds are 934, 1320 and 100, respectively.

It is found that these materials are clearly improved as compared with ZnS: Cu, Cl, but they are not yet in practical use.

Thereupon, the present inventors conducted various researches for producing light-emitting material using rare-earth element Eu as the light-emitting material. Based on the researches, the present inventors found that a light-emitting material having a new crystallization structure was obtained by adding an appropriate amount of B and an additive exciting agent. This light-emitting material has a desired long afterglow time and high brightness.

Therefore, a first object of the present invention is to provide a light-emitting material having a long afterglow time and high brightness.

Moreover, a second object of the present invention is to provide a producing method of the above-mentioned light-emitting material.

DISCLOSURE OF THE INVENTION

To achieve the objects, the present invention provides the following light-emitting material and the producing method.

That is, a light-emitting material of the present invention includes a diplophase compound crystallization expressed in a general formula: $(Sr, Eu, Dy)_{0.95\pm x}(Al, B)_2O_{3.95\pm x}\cdot(Sr, Eu, Dy)_{4-x}(Al, B)_{14}O_{25-x}$ $(x=0.01 \sim 0.1)$.

This diplophase compound has a new crystallization structure and consists of two phases, i.e., $(Sr, Eu, Dy)_{0.95\pm x}(Al, B)_2O_{3.95\pm x}$ and $(Sr, Eu, Dy)_{4-x}(Al, B)_{14}O_{25-x}$. This conclusion was obtained from XRD (X-ray diffraction) analysis using a Chinese geological university material scientific divisional crystallization structure and a large amount of samples carried out in a crystallization chemical laboratory. Based on the XRD analysis, and using an optical microscope and electronic probe analytical technique, it is corroborated that the above two phases are symbiosis and have light-emitting function.

The producing method of the light-emitting material includes the following steps:

(1) step for measuring previously pulverized raw materials, and mixing them to obtain a mixture of raw material,

(2) step for putting the mixture into a container, heating the mixture from 850℃ to 1200℃ for three hours under a reduction condition, keeping the temperature for five to six hours, thereby obtaining a sintered body,

(3) step for stopping the heating operation and cooling the sintered body nature down to a room temperature, and

(4) step for pulverizing the sintered body to obtain a product.

According to the light-emitting material and the producing method of the present invention, there is a light-emitting effect that which visible long afterglow ability as compared with a similar light-emitting material.

BEST MODE FOR CARRYING OUT THE INVENTION

In an assessment process concerning a phase of a light-emitting material of the present invention, using analytic means such as an X-ray fluorescent analysis, a plasma spectral analysis, electronic probe and X-ray photoelectron

energy spectrum, it was confirmed that a content of B element in diplophase compound is 0.2~1.0 % by weight in general, and variable ranges of contents of Eu element and Dy are from 0.5 to 3.0 % by weight and from 0.01 to 3.0 % by weight, respectively.

The element B exists in the entire crystallization structure. Moreover, the element B exists in a form of B-O tetrahedral coordination or BO_3 triangular coordination. The BO_3 Triangular coordination can substitute a portion of Al-O octahedron and this causes instability in the crystallization structure. This is an important structural feature of the light-emitting material of the present invention.

Further, the Al-O octahedron and Al-O tetrahedron concurrently exist in the diplophase compound crystallization of the present invention, and form a substantially hexagonal ring and positive ions of Sr, Eu and Dy are charged into a cavity of the ring. From the viewpoint of the entire crystallization diplophase compound, Al exists excessively and (Sr, Eu, Dy) are insufficient.

The raw materials which is used for the producing method of the light-emitting material of the present invention are $SrCO_3$, Al_2O_3, H_3BO_3, Eu_2O_3 and Dy_2O_3, of which, Eu3+ of Eu_2O_3 is reduced by Eu2+ during sintering process to excite the diplophase compound and provide the same with a light-emitting function. Dy_2O_3 strengthens the exciting effect of Eu_2O_3 as an additive exciting agent.

The term "reduction condition" used in the present invention means to reduce the above-mentioned mixed raw material using carbon powder, or to reduce the mixed raw material using mixture gas of nitrogen and hydrogen of volume ratio of 4:1. The light-emitting material produced by the invention has faint yellow-green color. When this light-emitting material is irradiated with sunlight, a fluorescent light or the other artificial light source and excited, the main peak of the light-emitting spectrum is 505 μm, and shows

blue or green.

As a result of measurement of samples, it was found that the light-emitting material of the present invention showed brightness of about 8500mcd/m^2 after five seconds from the instant when the irradiation was stopped, and visible afterglow time was 80 hours or longer (see Table 1). As shown in Table 1, the light-emitting material produced by the method of the present invention has especially excellent visible afterglow time.

The brightness is measured by the following method. That is, 0.2g of sample is put in a plastic plate of 10mm diameter and it is irradiated for 15 minutes from a perpendicular distance of 20cm using a fluorescent light of 15w at a room temperature and under humidity of 25RH%, and brightness of each sample is measured at various time points using an luminance meter (TOPCONBM-5, Japan TOPCON Inc.).

The light-emitting material produced by the method of the present invention has apparently long afterglow time in comparison with similar other products. Therefore, this material can suitably be applied to articles or safe sign which need to be seen in the dark, for example, a fireplug of a fire extinguishing tools and material, a handrail of safe stairs, and a road.

The following embodiments are for explaining the present invention in more detail, and are for limiting the invention.

[First Embodiment]

Previously pulverized 372.89g of $SrCO_3$, 220.32g of Al_2O_3, 12.616g of H_3BO_3, 2.42g of Eu_2O_3, and 0.157g of Dy_2O_3 were measured and sufficiently mixed. The mixed raw material was put into a container and it was covered with carbon powder, and heated from 850℃ to 1200℃ for three hours to increase it temperature, and the temperature was maintained for six hours. Then, the mixture was naturally cooled down to a room temperature to obtain a sintered body. The obtained sintered body was pulverized into such small pieces that all the pieces could pass through 200 mesh, thereby obtaining a product.

The product obtained in this manner had initial brightness of $3850mcd/m^2$ for 30 seconds and afterglow time was 85 hours. In the obtained produce, a value of x in the general formula was 0.01.

[Second Embodiment]

Previously pulverized 409.79g of $SrCO_3$, 220.32g of Al_2O_3, 12.616g of H_3BO_3, 2.96g of Eu_2O_3, and 0.164g of Dy_2O_3 were measured and sufficiently mixed. The mixed raw material was put into a container and it was covered with carbon powder, and heated from 850℃ to 1000℃ for three hours to increase it temperature, and the temperature was maintained for six hours. Then, the mixture was naturally cooled down to a room temperature to obtain a sintered body. The obtained sintered body was pulverized into such small pieces that all the pieces could pass through 200 mesh, thereby obtaining a product.

The product obtained in this manner had initial brightness of $3990mcd/m^2$ for 30 seconds and afterglow time was 80 hours.

In the obtained produce, a value of x in the general formula was 0.01.

Table 1

Measurement of brightness (mcd/m^2) and calculation of standard deviation

	Sample No.					Calculation of standard deviation		
Time	1	2	3	4	5	Average value	Standard deviation	Relative standard deviation
5 s	8400	8450	8400	8500	8500	8430	45	0.5%
10 s	7380	7570	7420	7410	7320	7460	125	1.8%
20 s	5120	5130	4930	5170	4870	5044	135	2.7%
30 s	4030	3960	3850	3990	3820	3930	91	2.3%
40 s	3380	3230	3160	3310	3110	3238	110	3.4%
60 s	2550	2490	2430	2490	2420	2476	53	2.1%
90 s	1870	1820	1780	1830	1750	1810	47	2.6%
3min	1520	1470	1460	1480	1420	1470	36	2.4%
4 min	870	850	840	840	820	844	18	2.1%
5 min	760	740	720	730	700	730	22	3.0%
3 min	630	630	610	610	590	614	17	2.8%
15 min	330	310	300	310	290	308	15	4.9%
30 min	160	150	140	140	130	144	15	8.3%
60 min	70	70	60	60	60	64	5.5	8.6%
90 min	50	40	40	50	40	44	5.5	12.5%
120 min	40	40	30	40	30	36	5.5	15.3%
180 min	20	30	20	20	20	22	4.5	20.5%
240 min	20	20	10	20	20	18	4.5	25.0%
360 min	20	10	10	20	10	14	5.5	33.6%
480 min	10	10	10	10	10	10	0	0